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RMD Report 5065-Q1  
Contract No. DA-11-070-AMC-852 (W)

## CARBORANE - SILOXANE ELASTOMERS

Report Period: 19 February 1965 through 18 May 1965

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*Thiokol*  
CHEMICAL CORPORATION  
REACTION MOTORS DIVISION  
DENVER, NEW JERSEY

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## FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, under U. S. Army Contract No. DA-11-070-AMC-852(W). It covers work done in the period 19 February 1965 through 18 May 1965. Contributors to the program are: Project Engineer, Mr. Z. T. Ossefort of Rock Island Arsenal, Illinois; Project Leader, Mr. Joseph Green of Thiokol; Principal Scientist, Mr. Nathan Mayes of Thiokol; Laboratory Technician, Mr. Alan Jackson of Thiokol.

### ABSTRACT

The synthesis of thermally stable carborane-siloxane elastomers was undertaken. Carborane and silane intermediates prepared include: neocarborane, 1,7-diallylcarborane, 1,7-bis[3-(chlorodimethylsilyl)propyl]carborane, tetramethyldisiloxane, dichlorotetramethyldisiloxane and chlorodimethylsilane. A liquid polymer was obtained by silyl hydride addition polymerization of 1,7-diallylcarborane and tetramethyldisiloxane. A homopolymer of 1,7-bis[3-(chlorodimethylsilyl)propyl]carborane prepared by hydrolysis, was obtained as a gum; copolymers of this compound with diethoxydimethylsilane and dichlorotetramethyldisiloxane, obtained by alkoxy-halogen condensation and hydrolysis respectively, were liquids of 1800 and 2500 molecular weight.

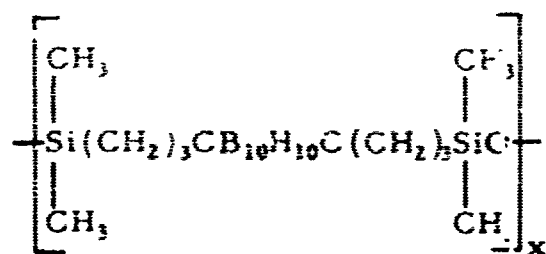
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## I. INTRODUCTION

The objective of this program is the synthesis of thermally stable carborane siloxane elastomers. Previous work to prepare carborane siloxane polymers has resulted in polymers containing carborane in the backbone and as pendant groups (Ref 1 and 2). These polymers were thermally stable to temperatures above 400°C as shown by TGA. They were also elastomeric when the carborane units, either backbone or pendant, were sufficiently spaced to permit chain flexibility. The structures with pendant carborane groups contained backbones that were wholly or primarily repeating siloxane groups and as such are capable of undergoing thermal rearrangement to form stable siloxane cyclic compounds. Moreover, the previously prepared backbone-carborane siloxane polymers were potentially hydrolytically unstable due to the presence of silicon-carborane linkages which, in analogous monomeric compounds, have been shown to be readily hydrolyzed.

The choice of structures to be investigated on this program was influenced by the foregoing considerations and as a result the structure considered to be most favorable for the objective is:



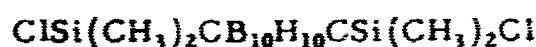
In this structure, there are no silicon-carborane bonds that may be hydrolyzed, repeating siloxane linkages are minimized to inhibit decomposition through cyclic siloxane formation, the thermal stability of the  $\text{Si}(\text{CH}_2)_3\text{CB}_{10}\text{H}_{10}\text{C}-$  grouping has been demonstrated, non-cyclic-forming m-carborane (neocarborane) is employed, and the polymethylene and siloxane groups in the backbone should give flexible chains. Thus, this program is directed toward preparation of polymers having the favored structure and variations of this structure in order to determine how factors such as number of repeating siloxane groups, number of methylene groups, or the regularity of the backbone structure affect thermal and physical

properties. Further study of pendant carborane siloxane polymers is also anticipated, primarily for comparison purposes.

The program consists of four phases: (1) synthesis of monomers and polymers, (2) curing studies, (3) evaluation of materials and (4) material supply. The monomers being synthesized in Phase I are compounds that will permit backbone-carborane polymer formation. The carborane monomers that have been or will be prepared are 1,7-diallylcarborane (I), 1,7-bis(chlorodimethylsilyl)carborane (II), and 1,7-bis[3-(chlorodimethylsilyl)propyl]carborane (III). The structure and numbering system of carborane are illustrated in Figure 1. The 1,7 isomer (neocarborane) is shown; other isomers are the 1,2(orthocarborane) and the 1,12 (paracarborane) structures.



I



II



III

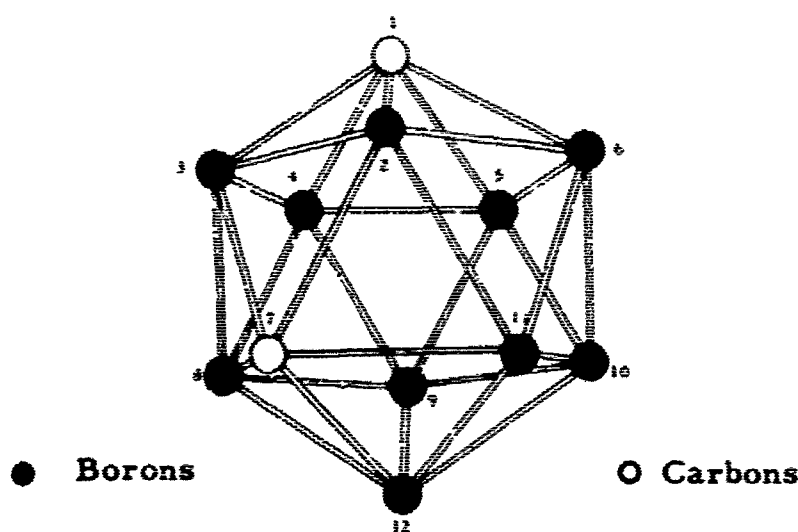
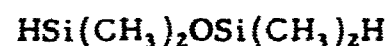
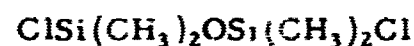


Figure 1. Structure and Numbering System of Carborane

Other compounds prepared are tetramethyldisiloxane (IV), dichlorotetramethyldisiloxane (V), and dimethylchlorosilane (VI). It was anticipated that chlorodimethylsilane could be purchased; however, this compound, which was commercially available from Dow-Corning up until a few months before the start of this program, is now unavailable and must be prepared in the laboratory.



IV



V



VI

The polymer synthesis employed three types of reactions. One type, hydrolysis and condensation of chlorosilanes or alkoxy silanes, is being used to prepare random polysilmethylenecarborane-siloxane copolymers. The other types, silyl hydride addition to a diolefin and alkoxy-halide condensation, are being used to synthesize regularly alternating polysilmethylenecarborane-siloxane copolymers.

The curing studies phase of the program will encompass investigation of peroxide curatives to form thermally stable ethylene crosslinks by hydrogen abstraction from pendant methyl groups. In addition, curing studies will be conducted with such curatives as  $\text{As}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{VOCl}_3$  and  $\text{Cr}_2\text{O}_3$  to form thermally stable Si-O-Metal crosslinks. Polymers that contain SiH will be cured at these sites to obtain Si-O-Si or SiC linkages.

Evaluation of materials will include initial characterization to determine molecular weight and polymer structure. Further evaluation will involve screening of the elastomer gum for thermal stability by TGA and DTA, and subsection of promising vulcanized products to TGA, DTA and standard ASTM heat aging tests to determine thermal and physical properties.

The materials supply phase of the program is for the purpose of preparing and supplying to the contracting agency 200 gram quantities of materials that have potential for meeting the goals of the program.



## II. TECHNICAL PROGRESS

### PHASE I - MONOMER AND POLYMER SYNTHESIS

#### A. Carborane Intermediates and Monomers

1,7-Diallylcarborane is necessary for the preparation of several of the polymer structures that have been proposed for this program. Although this compound has not been previously synthesized its isomer, 1,2-diallylcarborane, has been prepared (Ref 3) and the same procedure has been used here to synthesize the 1,7 isomer. m-Carborane was a starting material in this synthesis. It was prepared in a series of steps involving o-carborane preparation by oxidation of 1,2-bis(hydroxymethyl)carborane (Ref 4) and finally thermal isomerization of o-carborane to m-Carborane (Ref 5). m-Carborane was converted to the diallyl compound by reactions illustrated in Equations 1 and 2.



The reactions progressed smoothly to yield 89-92% of distilled product (yield based on m-carborane). The product is a colorless liquid of bp 63°C/0.15 mm and  $n_D^{20}$  1.5335. It was characterized by infrared and elemental analysis.

Calculated for  $\text{C}_8\text{H}_{20}\text{B}_{10}$ : C, 42.82; H, 8.98; B, 48.18

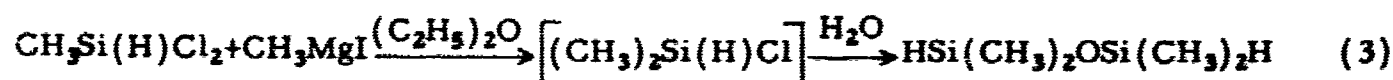
Found: C, 42.72; H, 8.87; B, 48.17

Approximately 130 g of 1,7-diallylcarborane was prepared in three separate reactions.

## B. Silane Intermediates and Monomers

### 1. Tetramethyldisiloxane

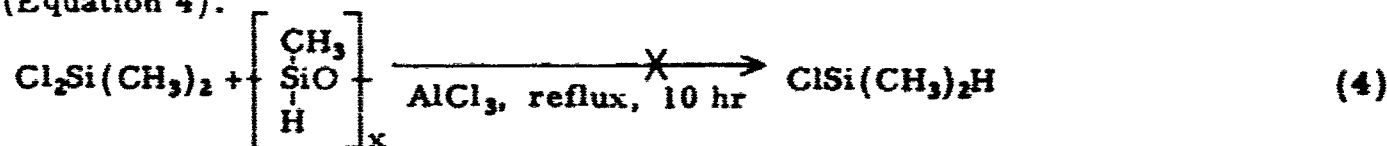
An attempt was made to prepare tetramethyldisiloxane by a Grignard reaction of methylmagnesium iodide with dichloromethylsilane followed by hydrolysis and fractional distillation of the products (Equation 3).



A product of bp 70°C (bp of tetramethyldisiloxane is 71°C, Ref 6) was obtained in 15% yield. The product was iodine-colored and apparently impure. A second attempt using methylmagnesium bromide as methylating agent yielded 50% of colorless product of bp 72°C and  $n_D^{20}$  1.3694 (Lit.  $n_D^{20}$  1.3700, Ref 6). Proton nuclear magnetic resonance analysis indicated the product to be tetramethyldisiloxane; however, infrared analysis and quantitative analysis for SiH indicated the presence of an impurity which was not identified.

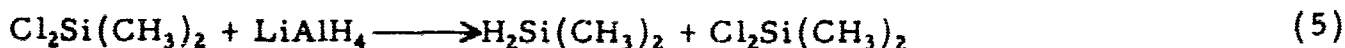
### 2. Chlorodimethylsilane

An effort was made to prepare chlorodimethylsilane by silicon halide-silicon hydride interchange reactions as suggested by Eaborn (Ref 7). Eaborn cites an example of silicon halide-silicon hydride interchange in which chlorodiethylsilane is obtained from the aluminum chloride catalyzed reaction of triethylsilane and dichlorodiethylsilane, and he suggests that a similar reaction could occur using the polysiloxane  $\left[ \begin{array}{c} \text{CH}_3 \\ | \\ \text{SiO} \\ | \\ \text{H} \end{array} \right]_x$  as a hydrogen source in place of triethylsilane. The suggested approach is attractive for the preparation of chlorodimethylsilane because of the ready availability of the hydrogen source (hydrolysis of  $\text{Cl}_2\text{Si}(\text{CH}_3)_2$ ) and because the product should be easily isolated. The reaction was attempted as suggested, however, none of the desired product was obtained (Equation 4).



The preparation of chlorodimethylsilane was accomplished by reduction of dichlorotetramethyldisiloxane with lithium aluminum hydride. It has been reported in several instances that partial reduction of organohalogen silanes is not possible (Ref 8). Thus, one cannot expect to reduce dichlorodimethylsilane

to chlorodimethylsilane. Such reactions actually yield the fully-reduced silane even when a considerable deficiency of lithium aluminum hydride is used (Equation 5).

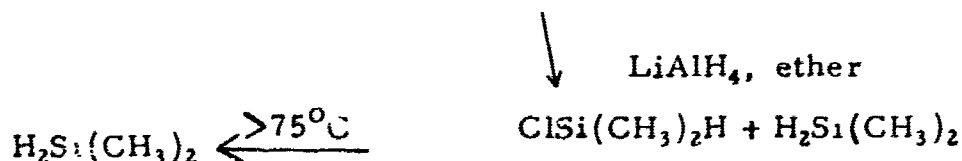
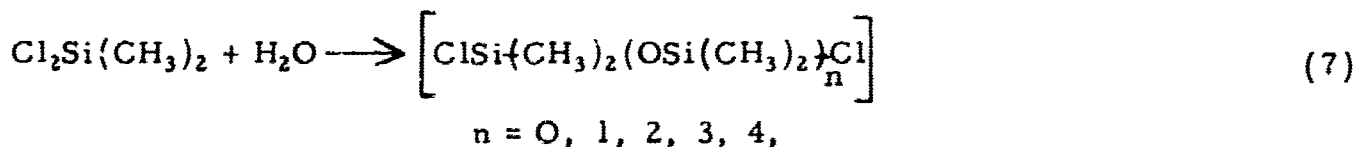


A variation of this reaction was done here in which the dichlorodimethylsilane was first partially hydrolyzed to dichlorotetramethyldisiloxane and then reduced with lithium aluminum hydride in ether solution. Reduction occurred preferentially at the siloxane bonds to yield chlorodimethylsilane (Equation 6).



The product (bp 36°C) could not be separated from ether by distillation, but its presence in the distilled ether solution (bp 35°C) was indicated by the infrared spectrum which exhibited absorptions for SiH and SiCH<sub>3</sub>. The solution yielded acid on hydrolysis, and a titration, assuming all chlorosilane present to be chlorodimethylsilane, indicated that the latter had formed in 53% yield (based on lithium aluminum hydride). If reduction also occurred at silylchloride bonds the formation of dimethylsilane would be expected; however, no dimethylsilane was obtained in the reaction products.

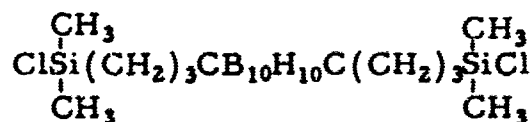
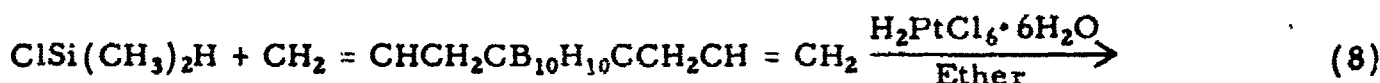
When the reaction was conducted using, instead of pure dichlorotetramethyldisiloxane, a mixture of dichlorosiloxanes obtained from the partial hydrolysis of dichlorodimethylsilane there was copious evolution of dimethylsilane. Chlorodimethylsilane also formed as it had previously; however, it was noted that distillation of the chlorodimethylsilane-ether solution proceeded smoothly at pot temperatures <75°C, but at higher pot temperatures, a reaction occurred to yield dimethylsilane (Equation 7).



The latter reaction was apparently a disproportionation between chlorodimethylsilane and hydrosiloxanes still present in the reaction mixture.

### C. Carborane-Silane Monomers

Chlorodimethylsilane, in ether solution, was allowed to react with 1,7-diallylcarborane (Equation 8), in the presence of chloroplatinic acid. Distillation

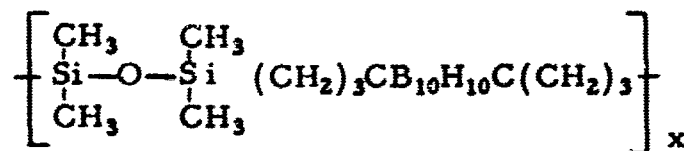
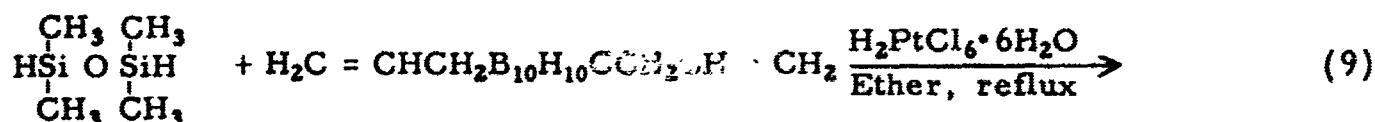


of the reaction mixture yielded a small quantity of unreacted 1,7-diallylcarborane and fractions that boiled at 135°C/0.04 mm and 155°C/0.05mm. The infrared spectrum of the lower boiling fraction indicated it to be the partial addition product,  $\text{H}_2\text{C} = \text{CHCH}_2\text{CB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{Cl}$ . The higher boiling material, on the basis of infrared and NMR analyses, is apparently 1,7-[bis(3-chlorodimethylsilyl)propyl]carborane.

### D. Polymers

#### 1. Silyl Hydride Addition Polymerization

The preparation of polymer by the reaction of tetramethyldisiloxane and 1,7-diallylcarborane was investigated (Equation 9).

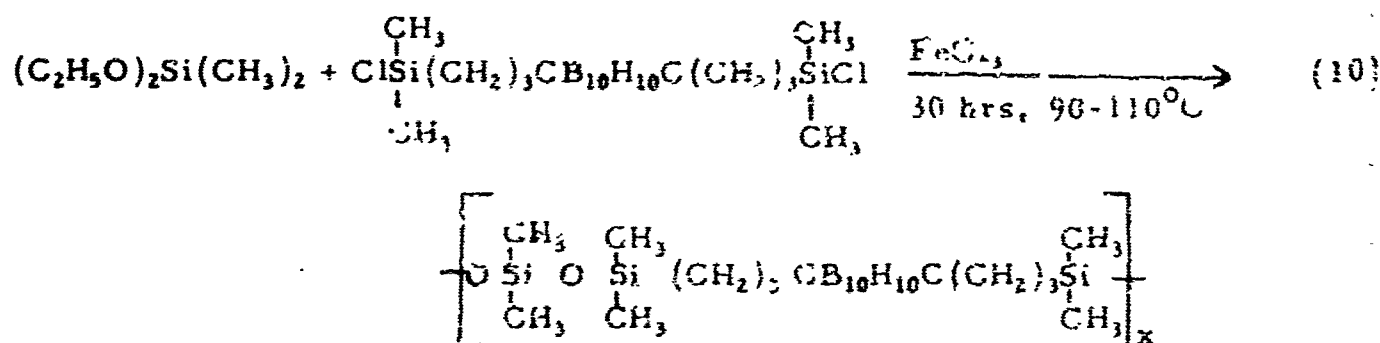


There was an exothermic reaction upon mixing the reactants in the presence of chloroplatinic acid. The product, obtained after refluxing in ether several hours, was a thin liquid apparently of low molecular weight. The infrared spectrum

showed loss of SiH and C = C and indicated that the addition had taken place.

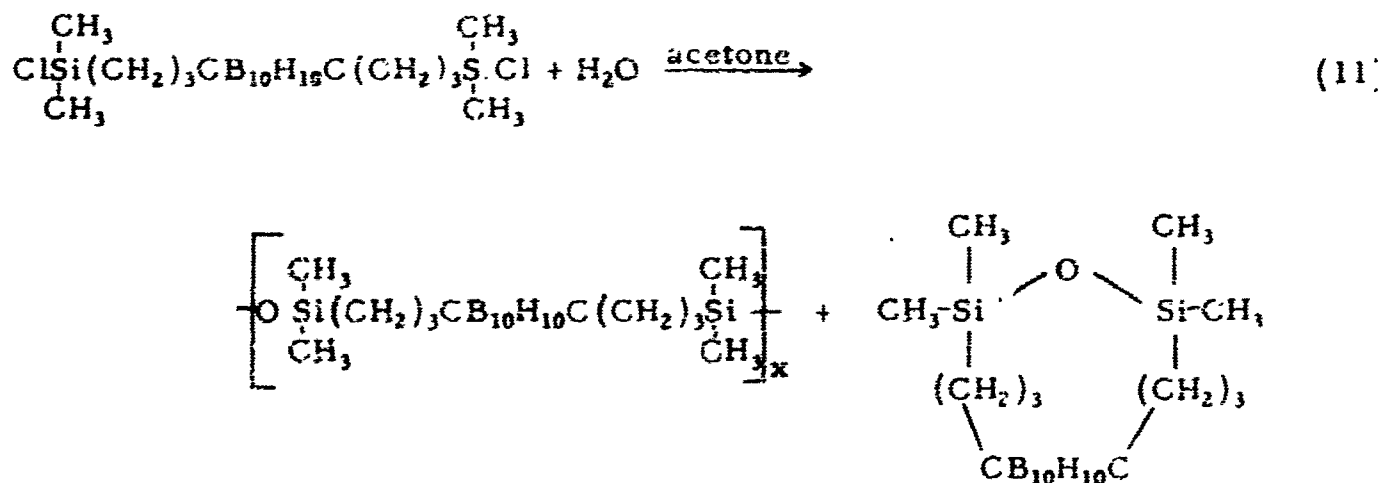
## 2. Alkoxysilane-Halosilane Condensation Polymerization

An attempt to prepare a regularly alternating copolymer by the ferric chloride catalyzed condensation of diethoxydimethylsilane and 1,7-bis [3-(dimethylchlorosilyl) propyl]carborane yielded a liquid product of 1800 molecular weight (Equation 10).

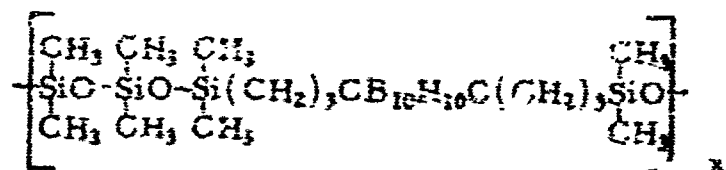
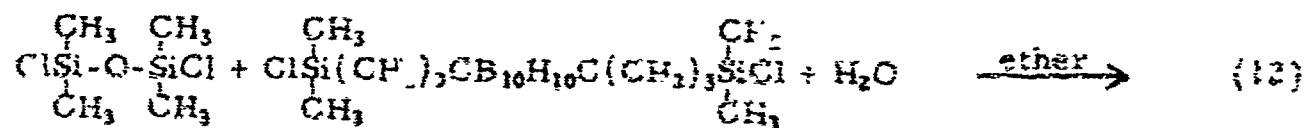


## 3. Hydrolysis/Condensation Polymerization

Polymerization of 1,7-bis [3-chlorodimethylsilyl) propyl] carborane by hydrolysis in acetone or methyl ethyl ketone solution yielded a clear colorless tacky gum and a small amount (<3%) of crystalline material that sublimed at 160-180°C/0.04mm (Equation 11). The sublimed material, upon examination by infrared and mass spectrographic analysis, appears to be a cyclic siloxane. The gum product is evidently polymeric; a molecular weight will be obtained.



A copolymer of 1,7-bis [3-(chlorodimethylsilyl) propyl]carborane and dichlorotetramethyldisiloxane was prepared by cohydrolysis of these two materials in ether solution. The product was a medium viscosity liquid of molecular weight 2500 (Equation 12).



### III. SUMMARY

This is a program to synthesize thermally stable carborane-siloxane elastomers. The polymer structure deemed most desirable for this objective is one having the grouping  $\text{-O} \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} \\ | \\ \text{CH}_3 \end{array} (\text{CH}_2)_3 \text{CB}_{10}\text{H}_{10} \text{C} (\text{CH}_2)_3 \begin{array}{c} \text{CH}_3 \\ | \\ \text{Si} \\ | \\ \text{CH}_3 \end{array} \text{-}$  in the chain backbone.

Toward the synthesis of such polymers, silane and siloxane intermediates and monomers have been prepared. These include chlorodimethylsilane, tetramethyldisiloxane, and dichlorotetramethyldisiloxane. The carborane materials, 1,7-diallylcarborane and 1,7-bis [3-(chlorodimethylsilyl)propyl] carborane, were prepared and their polymerization and copolymerization were investigated. A liquid polymer was obtained, by silyl hydride addition polymerization, from 1,7-diallylcarborane and tetramethyldisiloxane. A homopolymer of 1,7-bis-[3-(chlorodimethylsilyl)propyl] carborane was obtained as a gum; copolymers of this compound with diethoxydimethylsilane and dichlorotetramethyldisiloxane, obtained by alkoxy-halogen condensation and hydrolysis respectively, were liquids of 1800 and 2500 molecular weight.

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